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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Classification of clouds sampled at the puy de Dôme (France) from 10 yr monitoring: mean features of their physico-chemical properties" *by* L. Deguillaume et al.

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General comments

- The present manuscript describes 10 years of cloud chemistry observations at puy de Dome in France. It features an impressive dataset in terms of physical and chemical parameters measured and samples analyzed. Such large long term datasets of cloud chemistry are very rare and by themselves worthwhile additions to the scientific literature. The discussion of the results is very detailed but clear and organized

in a logical way. Some results like the importance of hydroxyacetaldehyde are rather novel while other observations are more expected/traditional. Overall the study is an interesting contribution to atmospheric chemistry and I would support publication of the manuscript while encouraging the authors to consider the following comments.

First of all, we would like to thank the reviewer for her/his interest in our work and the valuable remarks. We hope that our revised manuscript will satisfy the comments and corrections that were highlighted by the reviewer. In the revised manuscript, all the corrections are indicated by the red colour. We hope that this work may contribute to a better characterization of the chemical composition of the cloud medium.

- The measurements span over 10 years, or other long term fog and cloud studies showed significant changes in chemistry over such timeframes (e.g. Aleksic et al., 2009). Now, sulfur reduction happened likely before in France but one might wonder if there are still changes ongoing and if those could impact observations. The authors might want to address somewhere the potential for a temporal change.

In a first draft of this paper, we tried to extract temporal variations of some inorganic indicators (such as sulfate and nitrate for the pollution degree). By the way, no real trend was observed during the 10 years monitoring time scale. Regarding the suggested reference and data variations over the monitored period (i.e. Aleksic et al., 2009; over 12 years), no clear trend during this relative short period was found for the pH and the inorganic ions concentrations. In conclusion, we argue that possible trends can be extrapolated as a function of air mass origins (as reported in this work). In contrast to the gas phase monitoring where sulfur dioxide decrease is observed over the last 20 years, in the liquid phase, temporal variation cannot be clearly derived.

- About the methodology, do the authors know if the technique used quantifies only free aldehydes or also aldehyde/sulfite adducts (e.g. HMSA for formaldehyde). This would be interesting to know as the aldehyde concentrations could be lower estimates if they do not include HMSA and other adducts.

The technique used in the present work allows quantifying the free carbonyl concentrations. Indeed, HMSA and more generally S(IV)-carbonyl adducts form rapidly and are stable towards dissociation in acidic media such as cloud droplets. In this work, derivatization of carbonyls by DNSAOA was performed in an acidified (pH around 2) solution of the cloud sample. Dissociation of the carbonyl-S(IV) adducts in the course of the derivatization reaction is therefore unlikely, and carbonyl concentrations reported in this paper would represent the free carbonyl concentrations. A short paragraph has been included in the new version of the manuscript to avoid confusion. To illustrate this point of interest, 3 new references have been cited:

Dasgupta, P. K., DeCesare, K., and Ullrey, J.: Determination of atmospheric sulfur dioxide without tetrachloromercurate(II) and the mechanism of the Schiff reaction, Analytical Chemistry, 52, 1912-1922, 1980.

Munger, J. W., Jacob, D. J., and Hoffmann, M. R.: The occurence of bisulfite-aldehyde addition products in fog- and cloudwater, Journal of Atmospheric Chemistry, 1, 335-350, 1984.

Ang, C. C., Lipari, F., and Swarin, S. J.: Determination of hydroxymethanesulfonate in wet deposition samples, Environmental Sciences and Technology, 21, 102-106, 1987.

- The statistics methodology could benefit from some more details. May be the authors could specify if they really used straight PCA or may be some rotation? Or other transformation? Also it is not completely clear to this reviewer what a hierarchical classification is? Cluster analysis run by a statistics package? Finally it says that all data were included with 1 missing value maximum. How were the missing values treated?

Yes, we totally agree with this remark. In this work, we used a "straight" PCA without rotations. We used in the submitted manuscript the term "hierarchical classification" that is unclear. The right term is "hierarchical clustering analysis (HCA)" where cloud events or groups of cloud events are grouped together in pairs due to their similarities.

The cluster analysis didn't use a specific statistics package because the statistical analysis was performed with the Simca software. A very important problem in applications of PCA, such as multivariate statistical process control applications, is the estimation of scores when the observation vector has missing data. Simca's approach to score calculations for such incomplete observations are based on methods described in :

Nelson, P.R.C., Taylor, P.A., MacGregor, J.F.: Missing data methods in PCA and PLS: Score calculations with incomplete observation, Chemometrics and Intelligent Laboratory Systems, 35, 45-65, 1996.

These methods perform reasonable well with moderate amounts of missing data (up to 20% of the measurements). In our case, only 1 missing value is permitted that should lead to low errors.

- One detail is also that while principal component analysis does not strictly require data normality, a very skewed data distribution can result in PCA artifacts. Some statement on how this is or is not an issue might be useful.

To our opinion, regarding the high number of cloud samples and the relative low number of variables used for the PCA analysis, we can argue that the lack of data normality should generate few artifacts. This statistical technique was previously used for cloud water data for analyzing the effect of air masses transported over different regions (Deninger and Saxena, 1997; Kim et al., 2006).

Deininger, C. K., and Saxena, V. K.: A validation of back trajectories of air masses by principal component analysis of ion concentrations in cloud water, Atmospheric Environment, 31, 295-300, 1997.

Kim, M.-G., Lee, B.-K., and Kim, H.-J.: Cloud/fog water chemistry at a high elevation site in South Korea, Journal of Atmospheric Chemistry, 55, 13-29, 10.1007/s10874-005-9004-8, 2006b.

- For the least the term correlation in the context of PCA should be changed. I com-

mend the authors though for their approach to other correlation tests because of the non normality.

We agreed with this remark and removed the term "correlation" from the PCA description.

- Linking the differentiation between "marine" and "highly marine" to an elevated pH is a little debatable especially if one sees in the table that as the range of pH stretches higher in the marine category and one wonders if there is really a difference between the two in pH?

We classify cloud samples as highly marine when the amount of Na+ and Cl- are significantly higher than in comparison to "marine" air masses. The cloud samples that are classified as "marine" exhibit low concentration of these ions but elevated pH in comparison to cloud samples considered as "continental". Therefore, the pH is not the parameter that is relevant and used in this work to distinguish "marine" and "highly marine" clouds.

In order to clarify this point, we modified the sentences as following (page 9, line 28) : "The first one, classified as "highly marine", is characterized by high concentrations of Na+ and Cl- (means of 311 and 232 μM, respectively) while for the second group, classified as "marine", a low concentration of these ions is found. For both clusters ("marine" and "highly marine"), the pH range is closed."

- The comparisons to other studies are interesting. It should be noted though that sometimes different timeframes are compared (cf. also comment on evolution), e.g. a pH of 2.4 at Whiteface Mountain is cited but this was in the 1990s,... Recent work shows pH > one unit higher at this site (Aleksic et al., 2009). So the difference looks less substantial if similar timeframes are being compared.

We agree with your comment. Nevertheless, regarding the work from Aleksic et al. (2009) at Whiteface Mountain, the paper shows no significant variation in the pH values

between collected cloud waters from 1994 up to 2006. For this reasons, we considered that the cited work from Collett et al. (2002) is helpful to compare our minimal value (3.1) with those reported by the authors. In conclusion, we can argue that closed average pH values were found in our work at puy de Dôme (4.3) and those reported by the two cited papers (around 4) for polluted cloud samples.

A new sentence was added in the text (page 11, line 23) :

"Regarding the work of Aleksic et al. (2009) at the Whiteface Mountain during 12 years from 1994 to 2006, no significant pH variations (closed to 4) were reported over this period."

- On the other hand one wonders why the study does not compare itself then against the old French studies in the Vosges Mountains (e.g., Lammel and Metzig, 1991; Herckes et al., 2002).

In order to compare our results with previously reported French measurements, a new column was added in Table S2 where average concentrations of inorganic compounds were determined. In these works, sampled clouds present anthropogenic input clearly highlighted by elevated nitrate and sulfate concentrations. These two publications are now referenced and discussed in the text (page 14, line 14).

Details

- P22808: TOC discussion. "Remote" or background samples can also have high TOC because of local biogenic emissions e.g. Whistler in (Ervens et al., 2013). Hence may be mentioning of the season and/or lack of vegetation at pdD might be useful?

In Ervens et al. (2013), cloud and fog water were collected in Whistler (British Columbia, Canada), which represents a location that is influenced by a mix of anthropogenic and biogenic emissions. Nevertheless, in the present work, no seasonal variability (data are not reported) was noticed (see Figure 1 at the end that present TOC measurements as a function of the season). For these reasons we can argue

that no significant effect on the TOC content can be attributed to the vegetation around puy de Dôme station.

- In the text citations: may be cite multiple references in chronological order not random.

In our manuscript, we decided to classify our multiple references in alphabetical order ("the order can be based on relevance, as well as chronological or alphabetical listing"). Some multiple references were incorrectly classified and this is corrected in the revised version.

- The paper could benefit from some language editing:

- P22797 L20 replace interactions with interaction.

Done.

- P22803 L5 "." Not in right spot?

Done. We suppressed the "."

- P22804 L27 and throughout the text, please use only significant digits not 50.41% for a PC

Done.

- P22807 L25 "reducing" not "reducer"?

We replaced "oxidant or reducer" by "oxidizing medium or reducing one"

- P22810 L20: please provide a reference for "some studies"

Two references have been added in the revised manuscript.

- P22813 L21 "to our point of view" sounds odd

This was suppressed.

- P22816 L9 replace "underlined" by "highlighted"?

Done.

- P22818 L13 replace "followed" by "investigated"?

Done.

- P22818 L16 may be replaced "frame" with "framework"?

We replaced "frame" by "context".

- Table 1 and 2: please use only significant digits, e.g. Na+ concentration of 679 not 678.6.

Done.

- Table 3. if possible, please provide a number <X rather than BDL.

The limit of detection (LOD) is indicated now in the legend of Table 3.

- Figure 1: could you please put the fonts larger for the elements.

Yes, the fonts are really too small. We apologize for this. A new figure is now available with larger fonts.

Supplemental information

- Please also here use only significant digits in the tables. (e.g. 2193.00 looks odd).

Thanks a lot for this valuable remark. This is corrected in the new table.

- Please check formatting: some boxes didn't seem to have lines. Some boxes were shaded while others not. The references were not uniform (e.g. some with doi some not).

This has been corrected in the revised manuscript.

- References cited here:

N. Aleksic, K. Roya, G. Sistla, J. Dukett, N. Houck and P. Casson, Analysis of cloud

and precipitation chemistry at Whiteface Mountain, NY, Atmospheric Environment 43 (2009) 2709-2716.

P. Herckes, R. Wendling, N. Sauret, Ph. Mirabel and H. Wortham, Cloudwater studies at a high elevation site in the Vosges Mountains (France), Environmental Pollution, 117 (2002) 169-177.

G. Lammel and G. Metzig , Multiphase chemistry of orographic clouds: Observations at subalpine mountain stations, Fresenius J. Anal. Chem. 340 (1991) 564-574.

In the supplemental information, the table S2 has been completed to consider the measurements of these 3 studies. These 3 references have been added in the reference list.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 22795, 2013.

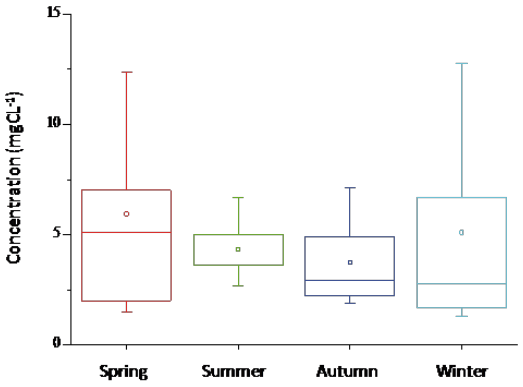

Fig. 1.